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The use of new modified poly(acrylamide) chelating resin with pendent benzothiazole groups containing donor atoms in the removal of heavy metal ions from aqueous solutions

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ABSTRACT

The adsorption studies of poly(6-(ethoxybenzothiazole acrylamide) (PEBTA), for Cu(II) and Zn(II) metal ions removal from an aqueous solution have been investigated, as a function of solution pH, adsorbent dose, contact time, initial metal ion concentration and temperature. The chemical and structural characteristics of the adsorbent were determined by the FT-IR, ^{1}H-NMR, TGA, SEM, and EDAX analysis. The maximum adsorption capacities of the adsorbent for Cu(II) and Zn(II) ions, as calculated from the Langmuir isotherm model, were 273.5 and 216.4 mg/g, respectively. The adsorption kinetic studies show that the adsorption of Cu(II) and Zn(II) ions onto PEBTA follows the pseudo second order kinetic model. Thermodynamic parameters such as ΔG°, ΔH° and ΔS° were also evaluated, and it has been found that the adsorption process is feasible, spontaneous and exothermic in nature. Desorption studies were carried out using 0.3 N HCl, and it revealed that the adsorbed Cu(II) and Zn(II) ions can be easily removed. The adsorption–desorption process is reversible, and

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this indicates that PEBTA is an effective adsorbent for the removal of heavy metal ions from an aqueous medium.

1. Introduction

Environmental pollution by toxic metals occurs globally, through waste disposal from agricultural processes, metallurgical, mining and electroplating industries. Among the environmental pollutants, heavy metals have gained relatively more significance, in view of their persistence and immense toxicity [1]. Heavy metals are non-biodegradable, can cause mental retardation, cancer and nervous system damage and, therefore, must be removed from water [2,3]. There are a number of methods in order to remove the heavy metal ions [4–8], including complexation, ion exchange, precipitation, reverse osmosis, extraction and adsorption. Adsorption is one of the most effective and easiest available methods for the removal of toxic heavy metals from aqueous systems. In the recent past polymeric adsorbents having emerging as potential alternative to activated carbon from various sources both agriculture and commercial. Polymeric adsorbents are superior to other solid adsorbents due to their vast surface area, adjustable surface chemistry, and feasible regeneration under mild conditions [9]. For the purpose of separation of metal ions either for purification or enrichment, various kinds of organic chelating resins have been developed. In general such chelating resins are co-ordinating co-polymers possesses covalently bonded side chains which contain single or multiple donor atoms. The donor atom containing active sites acts as Lewis base, which effectively forms co-ordinating bonds with Lewis acids such as the most toxic metal ions. Functional groups such as carboxylic [10,11], amide and amine [12], when present in the polymer structure, provide the binding sites for the removal of metal ions from aqueous solutions. Polymers with specific functionalities can be obtained, by either synthesizing new monomers bearing the functional groups capable of interacting with the target metal ions, followed by polymerization, or by converting the groups on the existing polymers or co-polymers with suitable chemical reactions into the desired functional groups [13,14]. Imidazo and amidoxime functional groups have been incorporated in the polymer back bone to adsorb various metal ions from aqueous solutions [15,16]. Polymers with methacryloyamido-glutamic acid and methacrylamide as the metal complexing ligand were synthesized and used for heavy metal ion removal [17,18]. New generation resins such as the one with bis-picolyamine functional groups were reported for selected metal ion adsorption from acidic solutions [19]. The aim of this study is to synthesize a new vinyl monomer bearing ethoxybenzothiozole pendant groups (which contains donor atoms N, O, and S), the preparation of its polymer, and finally to evaluate the new polymeric resin towards heavy metal ion adsorption. The efficiency of such chelating resins mainly depends on the types of resin functional groups and to a smaller extent on the resin bead size and physiochemical properties. For the first time we have attempted in the preparation and use of resins with pendent ethoxybenzothiozole complexing ligands. Batch adsorption studies were performed by varying parameters, such as solution pH, adsorbent dosage, contact time, initial metal ion concentration and temperature. Adsorption isotherms and kinetic models were used to predict the adsorption mechanism of Cu(II) and Zn(II) ions onto poly(6-(ethoxybenzothiazole acrylamide) PEBTA.

2. Materials and methods

2.1. Chemicals and reagents

Acrylic acid (Fluka) was used as received. Benzoyl chloride (E.Merck) was distilled rapidly before use. 2-Amino-6-(ethoxybenzothiozole) (Aldrich), benzoyl peroxide (Aldrich) were used without

further purification. 1-[Bis(dimethylamino)methylene]-1*H*-1,2,3-triazolo[4,5-*b*]pyridinium 1-oxide hexafluorophosphate (HATU) (Aldrich) and divinylbenzene (DVB) (Aldrich) were used as received. All the solvents viz., *N*-*N*′dimethylformamide (DMF) (Himedia, India), methylethylketone (MEK) (Himedia, India), methanol LR (Thomas Baker, India) and ethanol (Sakthi Sugars, India) were distilled once before use. $CuSO_4 \cdot 5H_2O$, $ZnSO_4 \cdot 7H_2O$ (AR grade) (SRL chemicals) were used for preparing the 500 mg/L stock solution, using double distilled water.

2.2. Monomer (6-(ethoxybenzothiazole)acrylamide)) (EBTA) synthesis

The synthesis of modified vinyl monomers using acryloyl chloride is a laborious and environmentally harmful process, due to the release of toxic vapors as by-products. Therefore, a new method using HATU condensation of acrylic acid with 2-amino-(ethoxybenzothiazole) was adopted, with a fairly good yield of the monomer. Typically, acrylic acid, 2-amino-6-(ethoxybenzothiazole), and triethylamine were taken in the mole ratio of 1.1:1.2:1 in a flat bottomed flask. The contents were mixed with 25 mL of DMF, and to this HATU was added at 0 °C and stirred at room temperature for 2–3 h. Powdered ice was poured into the solution, and a pale yellow solid was thrown out. It was stirred for a further half an hour, and allowed to settle at room temperature overnight. The solid monomer EBTA was filtered, washed with 0.1 N HCl to remove the un-reacted amine, washed with hot water, and finally with ethanol.

2.3. Polymer (poly(6-(ethoxybenzothiazole)acrylamide)) (PEBTA) synthesis

Radical polymerisation was carried out with benzoyl peroxide as the initiator. Divinylbenzene (DVB) of about 6% by weight of acrylamide monomer was added for the stability of the formed polymer. Into the polymerisation tube 3 g of monomer, 15 mL of MEK and 20 mL of DMF were added along with 50 mg of benzoyl peroxide and 0.2 mL DVB. The contents were flushed with oxygen free nitrogen for 30 min, and kept in a thermostat at 75 °C for 24 h. The contents were poured into acidified methanol. The polymer formed was emerged as a solid, which was filtered, washed several times with H_2O followed by ethanol, and dried under vacuum to a constant weight. The DVB stabilized PEBTA prepared, was used for adsorption studies. The repeat unit of polymer PEBTA is represented in Fig. 1.

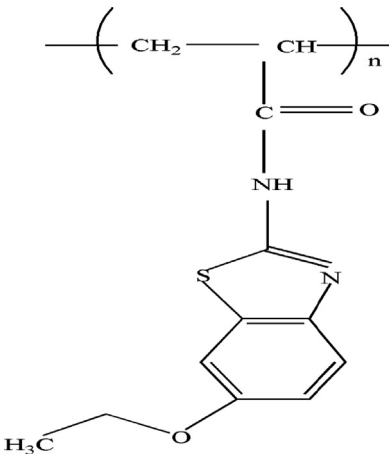

Fig. 1. Repeat unit of polymer (PEBTA).

2.4. Analytical method

The concentrations of Cu(II) and Zn(II) ions in the solution, before and after adsorption, were determined by AA6300 Atomic Absorption Spectrometer (Shimadzu, Japan). The pH of the solution was measured with a Hanna pH meter using a combined glass electrode. The EDAX analysis was carried out to confirm the adsorption of Cu(II) and Zn(II) ions onto the adsorbent, and the surface morphology of the adsorbent was studied, using the Leo Gemini 1530 Scanning Electron Microscope (SEM), at an accelerating voltage of 10 kV and at a working distance of 20 μm. The Fourier Transform Infra Red Spectrometer (FT-IR) analysis was used to identify the different functional groups present in the adsorbent and also to identify the functional group responsible for binding with metal ions in the aqueous solution.^{1}H-NMR spectra were recorded in DMSO-d_6, using a Bruker instrument. The Thermo Gravimetric Analysis (TGA) was done, using a Perkin-Elmer analyzer at a heating rate of 10 °C/min in static air.

2.5. Batch adsorption experiment

Batch adsorption experiments were carried out, by shaking the 20 mg of adsorbent PEBTA with 20 mL of 50 mg/L aqueous solution of metal ions, in a 250 mL conical flask, using a horizontal bench shaker (Orbiteck) at a constant speed of 200 rpm for 1 h at room temperature. By a systematic process, the removal of metal ions from the aqueous solution by the adsorbent in a batch system was studied. The data obtained in the batch studies were used to calculate the metal adsorptive capacity by using the following mass balance relationship:

$$q_e = \frac{(C_o - C_e)\,V}{m} \tag{1}$$

The metal ion removal percentage can be calculated as follows:

$$\%\,Removal = \frac{C_o - C_e}{C_o} \times 100 \tag{2}$$

where C_o and C_e are the initial and equilibrium concentrations (mg/L) of the metal ions, respectively, V (mL) is the volume of the metal ion solution, and m is the mass of adsorbent (mg).

3. Result and discussion

3.1. Characterization of adsorbent (PEBTA)

The FT-IR spectra of EBTA and polymer PEBTA are shown in Fig. 2(a) and (b), respectively. In the monomer Fig. 2(a) the peak at 3154 cm^{-1} is due to –NH stretching of the amide bond. The symmetrical and unsymmetrical stretching of the methylene groups are found at 3262 cm^{-1} and 2970 cm^{-1}, respectively. The carbonyl $>C=O$ stretching frequency is observed at 1652 cm^{-1}. The strong absorption band at 1516 cm^{1} is attributed to the $>C=C<$ stretching vibration of the olefinic double bond present in the monomer. The amine-II band is observed at 1476 cm^{-1}. In the FT-IR spectrum of polymer PEBTA the $>C=C<$ stretching vibration of the monomer (1516 cm^{-1}) is compared with the polymer. The $>C=C<$ olefinic stretching frequency is not seen in the FT-IR spectrum of the polymer. This clearly indicates that the vinyl group is involved in polymerization. In the polymer FT-IR spectrum, the carbonyl ($>C=O$) stretching frequency of the amide group is seen at 1681 cm^{-1}, and the amide-II bending frequency is observed at 1605 cm^{-1}. The –NH bending frequency appeared at 1501 cm^{-1}. From the FT-IR spectra of the monomer and polymer it can be deduced, that the olefinic $>C=C<$ has undergone polymerization reaction. The FT-IR spectra of the Cu(II) and Zn(II) ions adsorbed PEBTA are shown in Fig. 3(a) and (b), respectively. When compared with the raw polymer the IR spectra of Cu(II) and Zn(II) ions adsorbed polymer shows significant lower shifts in the carbonyl, amide II and –NH absorption frequencies. The carbonyl stretching frequencies of metal ion adsorbed polymer shows a lower shift of 17–28 cm^{-1}. Similarly the amide II

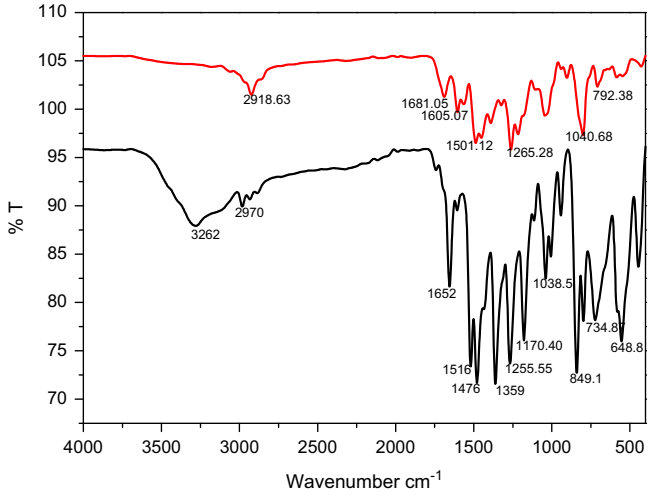

Fig. 2. FT-IR spectra of monomer EBTA (a) and polymer PEBTA (b), respectively.

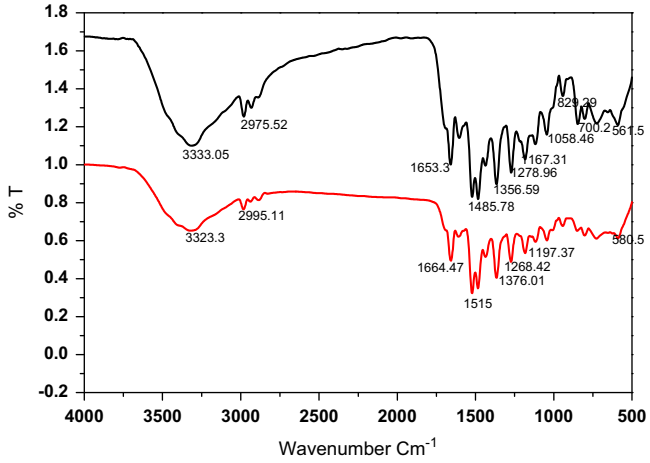

Fig. 3. FT-IR spectra of the Cu(II) (a) and Zn(II) ion adsorbed PEBTA (b).

absorption of the Cu(II) and Zn(II) metal ion adsorbed polymers appeared at 1515 cm^{-1} and 1520 cm^{-1}, respectively. When compared to the polymer the absorption amide II bands are shifted to a lower value. The –NH bending frequency also showed similar behaviors. These observations suggest that the amide carbonyl and the –NH groups are involved in complexation with the metal ions. The ^{1}H-NMR spectrum of the monomer EBTA is shown in Fig. 4(a). The peak observed at $\delta=7.5$ ppm is due to the pendent N–H protons, and the aromatic protons appear at $\delta=7.4$–7.0 ppm. The $-CH_2=CH-$ protons appeared at $\delta=4.2$ and 4.0 ppm. The pendent $-CH_2$ and $-CH_3$ protons were observed at $\delta=2.7$ and 1.3 ppm, respectively. The ^{1}H-NMR spectrum of the polymer stabilized with DVB is shown in Fig. 4(b). It is clearly seen that the spectrum of the polymer is ill-resolved, which is the first indication that the polymer has been formed. This is due to the entanglement of chains that distort the shielding effect. The N–H protons are confirmed by the peak at $\delta=7.4$ ppm. The aromatic protons appeared at $\delta=7.3$–7.0 ppm, and the $-CH_2-CH-$ protons were shown at $\delta=4.2$ and 4.0 ppm, respectively. The pendent CH_2 and CH_3 protons were observed at $\delta=2.6$ and 1.3 ppm, respectively. The thermal stability

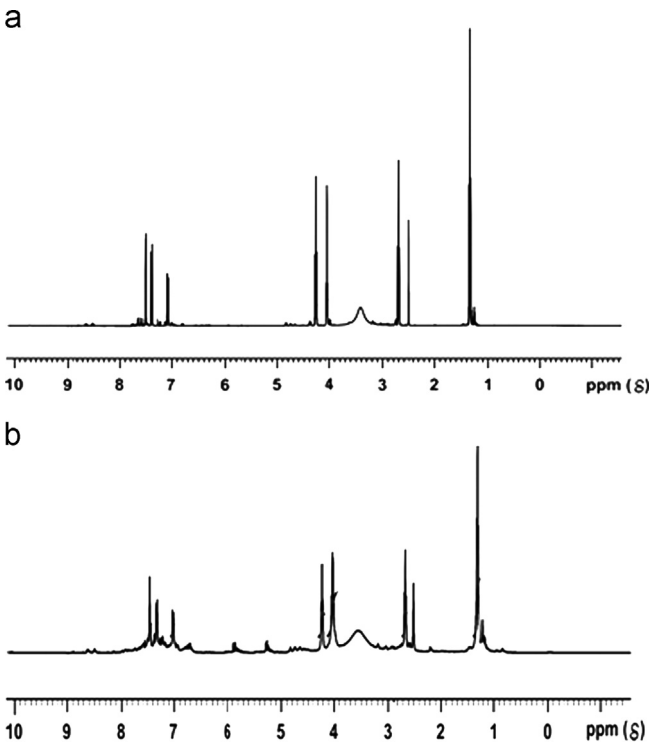

Fig. 4. ^{1}H-NMR spectra of monomer EBTA (a), polymer PEBTA (b).

of the polymer was evaluated using TGA. The polymer undergoes gradual degradation in the temperature range of 150–350 °C. The initial 10% weight loss may be attributed to the loss of the occluded solvent/non-solvent mixture. A further 10% weight loss occurs in the temperature range of 150–225 °C. The char yield at 700 °C is about 19.7%. The thermal history of the polymeric resin indicates that it can be used as an adsorbent up to 150 °C. The Scanning Electron Microscopic technique has been used to determine the surface morphology of the adsorbent. The SEM examination results of the adsorbent (PEBTA) are given in Fig. 5(a). From the image, it is clear that the adsorbent possesses highly irregular surface and pores, and these pores contribute to a very large surface area. The Cu(II) and Zn(II) metal ions adsorbed PEBTA are shown in Fig. 5(b) and (c), respectively. In the surface morphology of the Cu(II) and Zn(II) metal ion adsorbed PEBTA, the pores were filled thus confirming the adsorption process. The EDAX analysis was used to confirm the adsorption of the Cu(II) and Zn(II) metal ions onto the PEBTA adsorbent. Before the adsorption of the metal ions the EDAX image of the PEBTA shows only the peaks for the C, N, S and O atoms. After interaction with both the metal ions, two strong peaks appeared in the EDAX analysis for the Cu(II) and Zn(II) ions. This study further confirms that the Cu(II) and Zn(II) ions are successfully loaded onto the PEBTA surface.

3.2. Effect of solution pH on the adsorption of Cu(II) and Zn(II) ions onto PEBTA

During adsorption, the adsorbent acts as a weak base and co-ordinates with the metal atoms which are acidic based, on the Lewis acid–base principle. Therefore, solution pH is an important controlling factor that affects the surface charge of the adsorbent as well as the degree of ionization of different heavy metals. At a low pH, the H^{+} ions compete with the metal ions towards of the adsorption sites [20], and hence, a lower percentage removal of metal ions onto the adsorbent is observed. On the other hand, the percentage removal increases with an increase in the pH value, and

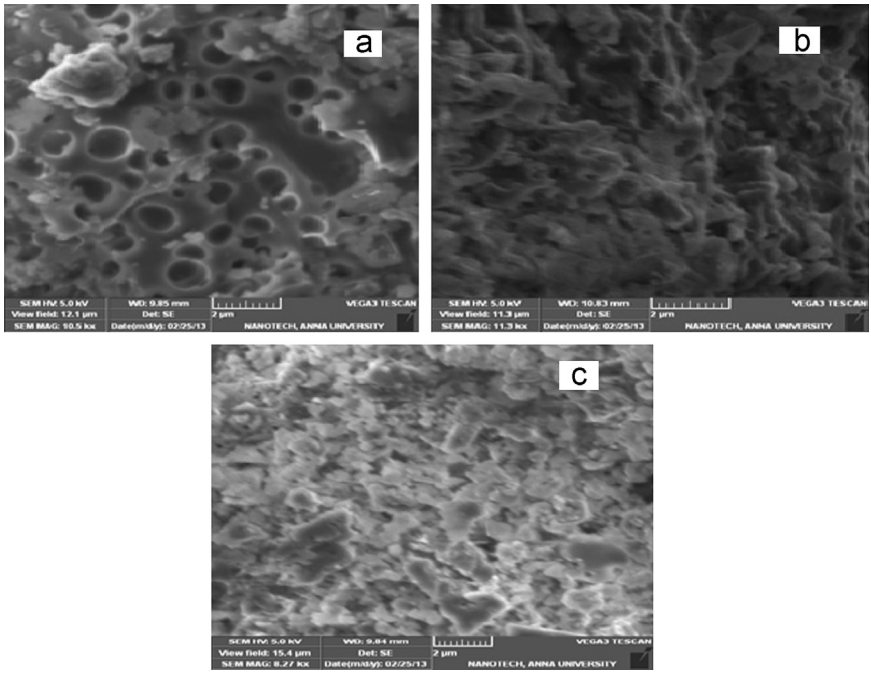

Fig. 5. SEM image of (a) PEBTA, (b) Cu(II) and (c) Zn(II) adsorbed PEBTA.

the percentage removal of Cu(II) and Zn(II) ions is almost complete at pH 6 (Fig. 6(a)). Beyond the pH value of 6 any further increase in pH results in a slight decrease in the percentage removal. This may be due to the formation of metal hydroxides. Hence, an optimum pH=6 was fixed for further adsorption studies.

3.3. *Effect of adsorbent dosage on the adsorption of Cu(II) and Zn(II) ions onto PEBTA*

Adsorbent dosage is an important factor for determining the adsorption capacity of an adsorbent. The percentage removal of Cu(II) and Zn(II) metal ions increases from 77.19 to 98.6% and 68.3 to 98.5%, respectively with an increase of PEBTA dose from 5 mg to 30 mg, at a pH 6, at room temperature for 1 h. The increase of % removal results from the higher number of adsorption sites available with higher dose of PEBTA, for the complexation of the metal ions. The percentage removal increases gradually till 30 mg, and shows no further increase (Fig. 6(b)). This suggests that, with a certain dose of PEBTA, the maximum adsorption is attained, which may be due to the saturation of all the adsorption sites on the surface of the adsorbent. Hence, an optimum adsorbent dosage of 20 mg was selected for further experiments.

3.4. *Effect of contact time on the adsorption of Cu(II) and Zn(II) ions onto PEBTA*

The effect of the contact time on the percentage removal of Cu(II) and Zn(II) ions from an aqueous solution using PEBTA was studied, and the results are shown in Fig. 6(d). The results show that the percentage removal of Cu(II) and Zn(II) increases with an increase in the contact time. The initial adsorption rate was fast due to the existence of greater numbers of resin sites are available for metal ion adsorption. Beyond 60 min with maximum removal of metal ions equilibrium is attained. Hence a 60 min contact time was selected for further experiments.

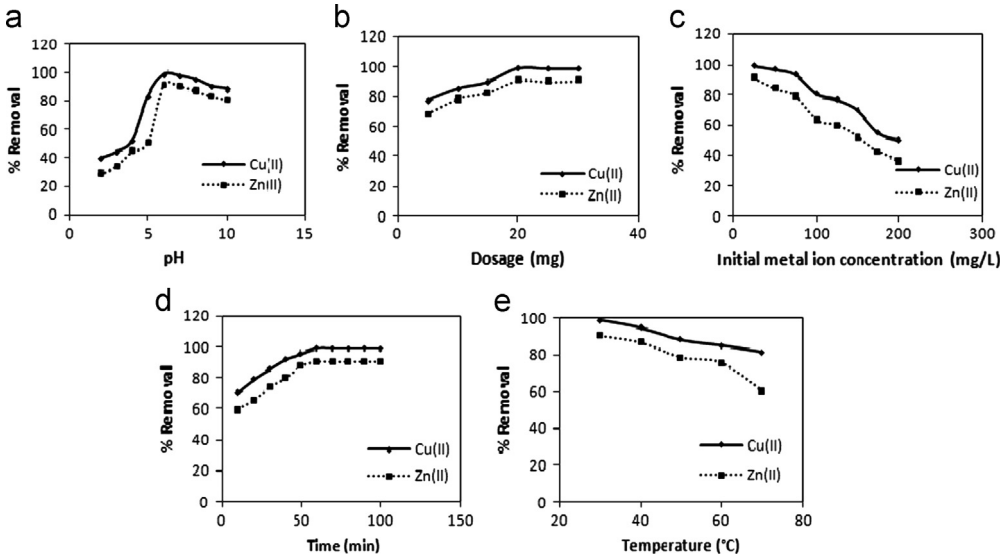

Fig. 6. Effect of pH (a), adsorbent dosage (b), time (c), initial metal ion concentration (d) and temperature (e) for the adsorption of Cu(II) and Zn(II) ions onto PEBTA.

3.5. *Effect of initial metal ion concentration on the adsorption of Cu(II) and Zn(II) ions onto PEBTA*

The initial metal ion concentration is one of the most important parameters for effective adsorption. These study was carried out under the optimum conditions of pH = 6, dosage = 20 mg, time = 60 min, temperature = 30 °C. The percentage removal decreases with an increase in the initial metal concentration from 25 mg/L to 100 mg/L. After 90 min the percentage removal decreases sharply, which may be due to the saturation of the adsorption sites, on the PEBTA. This is shown in Fig. 6(c). The higher percentage removal at lower concentrations may be due to the higher adsorption rate and availability of the adsorption sites. A decrease in the percentage removal beyond 90 mg/L may be due to the saturation of all the adsorption sites.

3.6. *Effect of temperature on the adsorption of Cu(II) and Zn(II) ions onto PEBTA*

The adsorption of Cu(II) and Zn(II) metal ions on to PEBTA was studied as a function of temperature. The experiments were carried out at five different temperatures viz., 30 °C, 40 °C, 50 °C, 60 °C and 70 °C, for the initial metal concentration of 50 mg/L, adsorbent dose 20 mg, time 60 min and at a pH of 6. Maximum percentage of metal ion removal was obtained at 30 °C, and at higher temperatures the adsorption capacity decreases (Fig. 6(e)). Temperature studies helps to predict whether the ongoing metal ion adsorption process is endothermic or exothermic in nature. The observation that the percentage removal of metal ions decreases with an increase in temperature indicates that the process is exothermic in nature [21] and no permanent chemical bonds are formed during adsorption.

3.7. *Adsorption isotherm*

The adsorption isotherm models show the distribution of metal ions between the liquid and solid phases, when the adsorption process attains the equilibrium stage. An analysis of the isotherm data is a significant one to find suitable model for adsorption design. The adsorption capacity of the present system was investigated with the Langmuir [22], Freundlich [23] and Temkin [24] adsorption isotherms.

The Langmuir isotherm is applicable to a homogeneous adsorption system while Freundlich isotherm assumes multilayer adsorption and heterogeneous adsorption surface with active sites. The Temkin isotherm explains the behavior of adsorption on heterogeneous surfaces. This model assumes that the heat of adsorption of all molecules decreases linearly, with coverage of the adsorbate/adsorbate interactions. The non-linear forms of the studied isotherm equation are expressed as follows:

$$q_e = \frac{q_m K_L C_e}{1 + K_L C_e} \tag{3}$$

$$q_e = K_f C_e^{1/n} \tag{4}$$

$$q_e = B\ln(AC_e) \tag{5}$$

where C_e is the supernatant concentration at the equilibrium state of the system (mg/L), q_m (mg/g) and K_L (L/mg) are the Langmuir constants, representing the maximum capacity for solid phase loading, and the energy constant related to the heat of adsorption, respectively. K_f is the Freundlich constant ((mg/g)(L/mg)$^{1/n}$) related to the bonding energy. K_f can be defined as the adsorption or distribution coefficient, and represents the quantity of metal ions adsorbed onto the adsorbent for unit equilibrium constant, $1/n$ is the heterogeneity factor, and n is a measure of deviation from linearity, between the solution concentration and adsorption. If $n=1$, then, the adsorption is linear; if $n<1$, then adsorption is a chemical process; if $n>1$, then adsorption is a physical process. $B=RT/b$, b is the Temkin constant related to the heat of adsorption (J/mol), A is the Temkin constant (L/g), R is the universal gas constant (8.341 J/mol/K) and T is the absolute temperature. All the constants are presented in Table 1.

Moreover in Langmuir isotherm dimensionless constant (R_L) is used to predict the affinity between the adsorbent and adsorbate, and the R_L value was calculated as follows:

$$R_L = \frac{1}{1 + K_L C_e} \tag{6}$$

where K_L is the Langmuir constant and C_o is the initial concentration of Cu(II) and Zn(II) ions, respectively. The value of the separation parameter R_L value gives important information about the nature of adsorption, when the R_L values are between 0 and 1; it shows that the adsorbent-metal system is favorable to the adsorption process. The Langmuir isotherm is said to be irreversible when ($R_L=0$), favorable if ($0<R_L<1$), linear when ($R_L=1$) and unfavorable if ($R_L>0$). The R_L values were found to be (0.1261 to 0.0175) for Cu(II)and (0.1384 to 0.0189) for Zn(II) ions in the range of 25 mg/L to 250 mg/L. This result indicates that the adsorption process is more favorable. The R_L values further confirm that PEBTA is a good adsorbent for the removal of Cu(II) and Zn(II) ions from an aqueous solution. The n value in the Freundlich equation was found to be 5.139 and 5.284 for Cu(II) and Zn(II) onto PEBTA. Since n lies between 1 and 10, the adsorption may be physical adsorption. All other parameters of the Freundlich isotherm models are presented in Table 1.

Based on its correlation coefficient values the isotherm fits are of the order Langmuir > Temkin > Freundlich isotherms for both Cu(II) and Zn(II) ions. It can be explained that the Langmuir isotherm has a better fit compared to the other two isotherm models, and this phenomenon suggests that the maximum monolayer adsorption takes place on the surface of the PEBTA, rather than a multilayer adsorption. The Isotherm results suggest that the maximum adsorption capacity (q_e) is higher for Cu(II) compared to Zn(II) ions on to PEBTA.

3.8. Adsorption kinetics

Kinetic studies are important to optimize different operation conditions for the adsorption of metal ions. This study reveals the rate of adsorption, and this rate controls the equilibrium. Pseudo first order [25], Pseudo second order [26], Elovich [27] and Intra particle diffusion kinetic models [28] were used with the experimental data.

Table 1
Isotherm parameters for the adsorption of Cu(II) and Zn(II) ions onto PEBTA.

Isotherm model	Parameters	Cu(II) ion	Zn(II) ion
Langmuir	K (L/mg)	0.2747	0.2586
	q_m (mg/g)	273.50	216.40
	R^2	0.9863	0.9502
Freundlich	K_f (mg/g)	112.60	90.140
	n	5.1390	5.2840
	R^2	0.7962	0.7749
Temkin	α (L/mg)	7.2700	7.2200
	β (mg^{-1})	18.300	14.320
	R^2	0.8672	0.8236

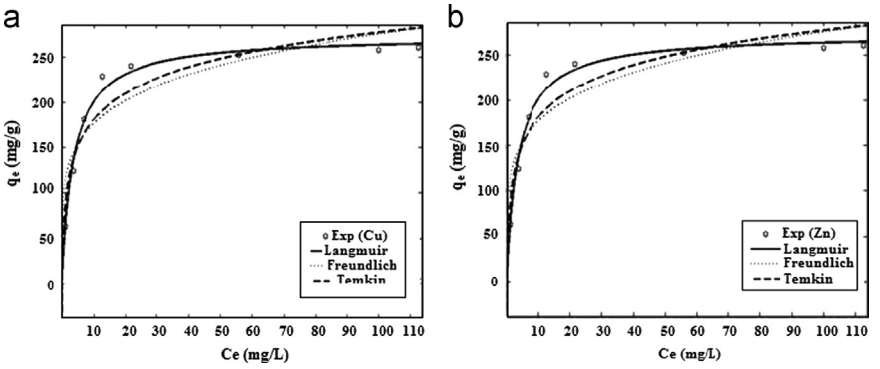

Fig. 7. Non-linear adsorption isotherm for Cu(II) and Zn(II) ions onto PEBTA.

The integral forms of the studied kinetic models are

$$log\ (q_e - q_t) = \log\ q_e - \frac{k_{ad}}{2.303} t \tag{7}$$

$$\frac{t}{q_t} = \frac{1}{h} + \frac{t}{q_e} \tag{8}$$

$$q_t = \frac{1}{\beta} ln(\alpha\beta) + \frac{1}{\beta} ln\ t \tag{9}$$

$$q_e = k_p t^{1/2} + C \tag{10}$$

where q_t and q_e are the adsorption capacity at time t (mg/g) and at equilibrium, respectively, and k_{ad} (min^{-1}) is the Pseudo-first order rate constant of the adsorption. A plot of log ($q_e - q_t$) versus t gives a straight line for the Pseudo-first order model and is shown in Figs. 7 and 8(a). $h = kq_e^2$ (mg/g/min) can be regarded as the initial adsorption rate as $t \to 0$, and k is the rate constant of Pseudo-second order adsorption (g/mg/min). Fig. 8(b) shows that the plot of t/q_t versus t gives a straight line, implying that the adsorption system studied follows the Pseudo-second order kinetic model. α and β are known as the Elovich co-efficient, α represents the initial adsorption rate in mg/(g/min), and β is related to the extent of the surface coverage and activation energy for chemisorption (g/mg), respectively. Both the kinetic constants (α and β) can be estimated from the slope and intercept of the plot of q_t verses ln$t$. The Cu(II) and Zn(II) ion adsorption kinetics onto PEBTA were also tested with the Elovich kinetic model, by plotting q_t versus lnt (Fig. 8(c)). C is the intercept and k_p is the intra-particle diffusion rate constant (g/m/$min^{1/2}$), which can be evaluated from the slope of the linear plot of q_t and $t^{1/2}$. The intra-particle diffusion straight line (Fig. 8(d)) does not pass through the origin. The initial curve

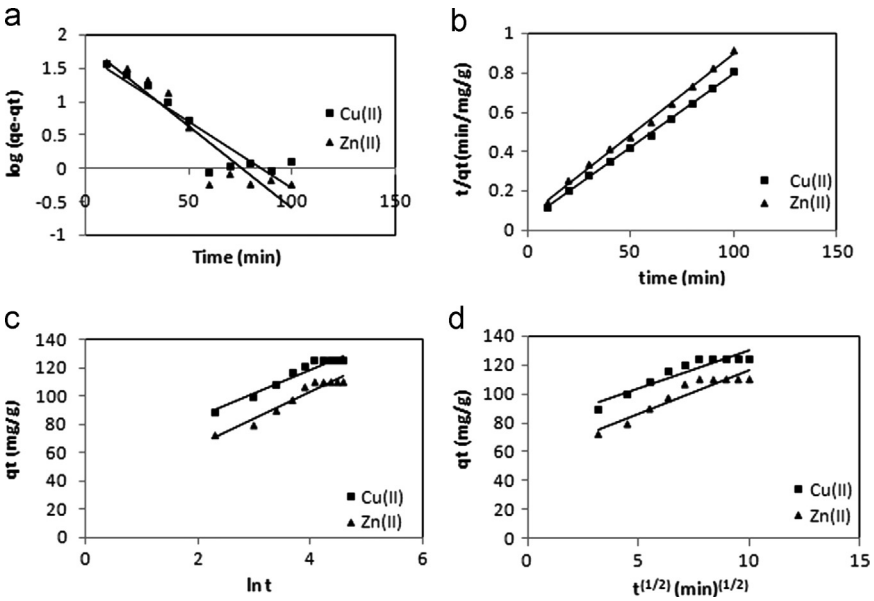

Fig. 8. Pseudo first order kinetic model (a), pseudo second order kinetic model (b), Elovich kinetic model (c) and Intra-particle diffusion model (d) for the adsorption of Cu(II) and Zn(II) ions onto PEBTA, respectively.

in the plot indicates a boundary layer effect and the second portion of the plot indicates the intra-particle diffusion. This shows that there is some degree of boundary layer control and this further indicates that the intra-particle diffusion is not the rate-limiting step, but adsorptions can also be involved in the rate limiting step or both may be operating simultaneously. The calculated values are presented in Table 2.

From the Pseudo-first order it is seen that, the values of $q_{e,\mathrm{exp}}$ are not comparable to the calculated values of $q_{e,\mathrm{cal.}}$ The values obtained from the Pseudo-second order model are close to the experimental $q_{e,\mathrm{exp}}$ values (Table 2). Moreover, based on the higher R^2 values, it can be concluded, that the adsorption of metal ions onto PEBTA followed the Pseudo-second order model rather than that of the Intra-particle diffusion, Pseudo-first order and Elovich kinetic models.

3.9. Thermodynamic studies

The study of the influence of temperature on adsorption with PEBTA has been investigated at 303 K, 308 K, 313 K, 318 K and 323 K. The thermodynamic studies of an adsorption process are necessary, to find out whether the adsorption process is spontaneous or not. Thermodynamic parameters, such as free energy (ΔG°), enthalpy change (ΔH°) and entropy change (ΔS°) were calculated from the following equation [29]:

$$K_c = \frac{q_e}{C_e} \tag{11}$$

$$\Delta G^\circ = -RT \ln K_c \tag{12}$$

$$\log K_c = \frac{\Delta S^\circ}{2.303R} - \frac{\Delta H^\circ}{2.303RT} \tag{13}$$

where K_c is the equilibrium constant, C_e is the equilibrium concentration in solution (mg/L) and q_e is the solid-phase concentration at equilibrium (mg/L). ΔG°, ΔH° and ΔS° are changes in Gibbs free energy (kJ/mol), enthalpy (kJ/mol) and entropy (J/mol/K), respectively. R is the universal gas constant (8.314 J/mol/K) and T is the temperature (K). The values of ΔH° and ΔS° were obtained from the slope

Table 2
Kinetic parameters for the adsorption of Cu(II) and Zn(II) ions onto PEBTA.

Kinetic model	Parameters	Cu(II) ion	Zn(II) ion
Pseudo-first order	k_{ad} (min^{-1})	0.0438	0.6220
	$q_{e,cal}$ (mg/g)	1.9590	32.584
	R^2	0.8450	0.8670
	$q_{e,cal}$ (mg/g)	142.86	125.00
Pseudo-second order	k (g/mg/min)	1.167×10^{-3}	0.914×10^{-3}
	h (mg/g/min)	23.82	13.06
	$q_{e,exp}$ (mg/g)	125.234	110.264
	R^2	0.998	0.9960
Elovich equation	α (mg/g/min)	20.70	81.750
	β (g/mg)	0.059	0.0533
	R^2	0.950	0.9390
Intra particle diffusion model	k_p ($mg/g/min^{1/2}$)	5.289	5.979
	C	77.60	56.74
	R^2	0.877	0.889

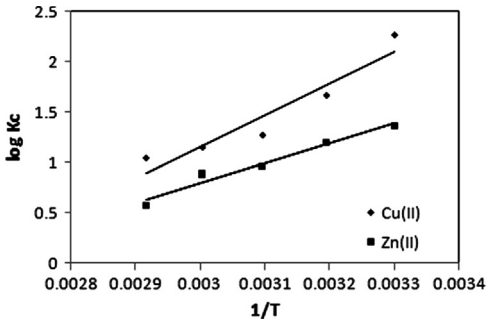

Fig. 9. Plot of log K_c against $1/T$ for the adsorption of Cu(II) and Zn(II) ions onto PEBTA.

and the intercept of the plot of log K_c versus $1/T$ (Fig. 9). The obtained thermodynamic parameters are presented in Table 3. The negative value of ΔH° suggests the exothermic nature of adsorption, and the negative values of ΔG° indicate the feasibility and spontaneous nature of the adsorption process. The ΔG° value is small and negative, but increases with an increase in temperature, indicating that the adsorption process leads to a decrease in Gibbs free energy. The negative values indicate that the metal adsorption was spontaneous and thermodynamically feasible. Negative ΔH° means a chemically exothermic process and hence chelating mechanism may generally dominate over ion-exchange mechanism.

3.10. Recyclability

The desorption studies are useful in elucidating the nature of the adsorption process and the potential application of the resin. Cu(II) and Zn(II) ion loaded PEBTA, was washed with double distilled water several times to remove unadsorbed metal ions. Then, it was treated with 50 mL solution of 0.3 N HCl for about 5 h; after that it was washed with distilled water to remove the acid present on the adsorbent surface, and used for further adsorption cycles. The adsorption–desorption cycles were repeated five times, and it was found that there was only a little change in the efficiency of Cu(II) and Zn(II) ions (adsorption–desorption) even after five cycles (Fig. 10). This suggests that the PEBTA resin is acid resistant, and the adsorbents had a good potential for re-use.

Table 3
Thermodynamic parameters for Cu(II) and Zn(II) ions adsorption onto PEBTA.

Parameter	Temperature (K)	Metal ion	
		Cu(II)	Zn(II)
$-\Delta H$ (kJ/mol)		59.72	37.49
$-\Delta S$ (J/mol)		156.97	97.13
$-\Delta G$ (kJ/mol)	303	12.18	11.07
	313	10.61	7.090
	323	9.040	6.117
	333	7.472	5.150
	343	5.903	4.110

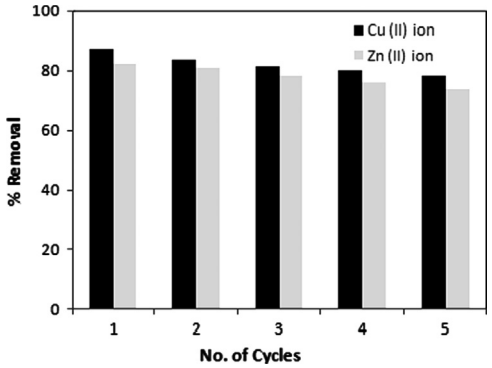

Fig. 10. Recyclability of PEBTA.

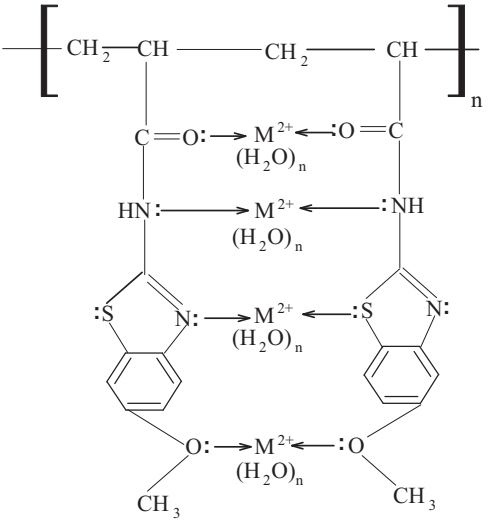

Fig. 11. Adsorption mechanism.

4. Conclusion

The following conclusions can be arrived at based on the study of Cu(II) and Zn(II) metal ions removal by the new polymeric adsorbent PEBTA. From the batch adsorption studies, the percentage removal of heavy metal ions was found to be dependent on the solution pH, dosage, initial metal ion concentration, time and temperature. It was observed that the Cu(II) and Zn(II) metal ions adsorption by PEBTA has the highest percentage removal at pH 6, while the maximum adsorbent dosage is 20 mg in 20 mL metal solution. The isotherm data of the Cu(II) and Zn(II) metal ion adsorption on PEBTA was analyzed by the Langmuir, Freundlich and Temkin isotherms. From the Langmuir isotherm model maximum adsorption capacity of PEBTA was found to be 273.5 and 216.4 mg/g for Cu(II) and Zn(II) ions, respectively. It is evident from the equilibrium adsorption data of Cu(II) and Zn(II) metal ions onto PEBTA the pseudo-second-order kinetic model finds the best fit. The thermodynamic studies indicate that the process was exothermic and spontaneous in nature. Based on the FT-IR, isotherms and kinetics a mechanism of adsorption is suggested in Fig. 11 where a co-ordinate bond between the donor atoms of the binding sites of the resin with M^{+2} ions. Finally, it can be concluded that PEBTA is a good adsorbent for the removal of heavy metal ions from aqueous solutions, due to its efficiency and recyclability.

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